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THE FREE ENERGY OF FORMATION OF THALLOUS
IODIDE.

THE CONDUCTIVITY AND IONIZATION OF THALLOUS NITRATE SOLUTION;
THE SOLUBILITY OF THALLOUS CHLORIDE AND OF THALLOUS IODIDE;
THE NORMAL POTENTIALS OF THE THALLIUM AND OF THE IODINE
ELECTRODES.

BY GRINNELL JONES AND WALTER CECIL SCHUMB.

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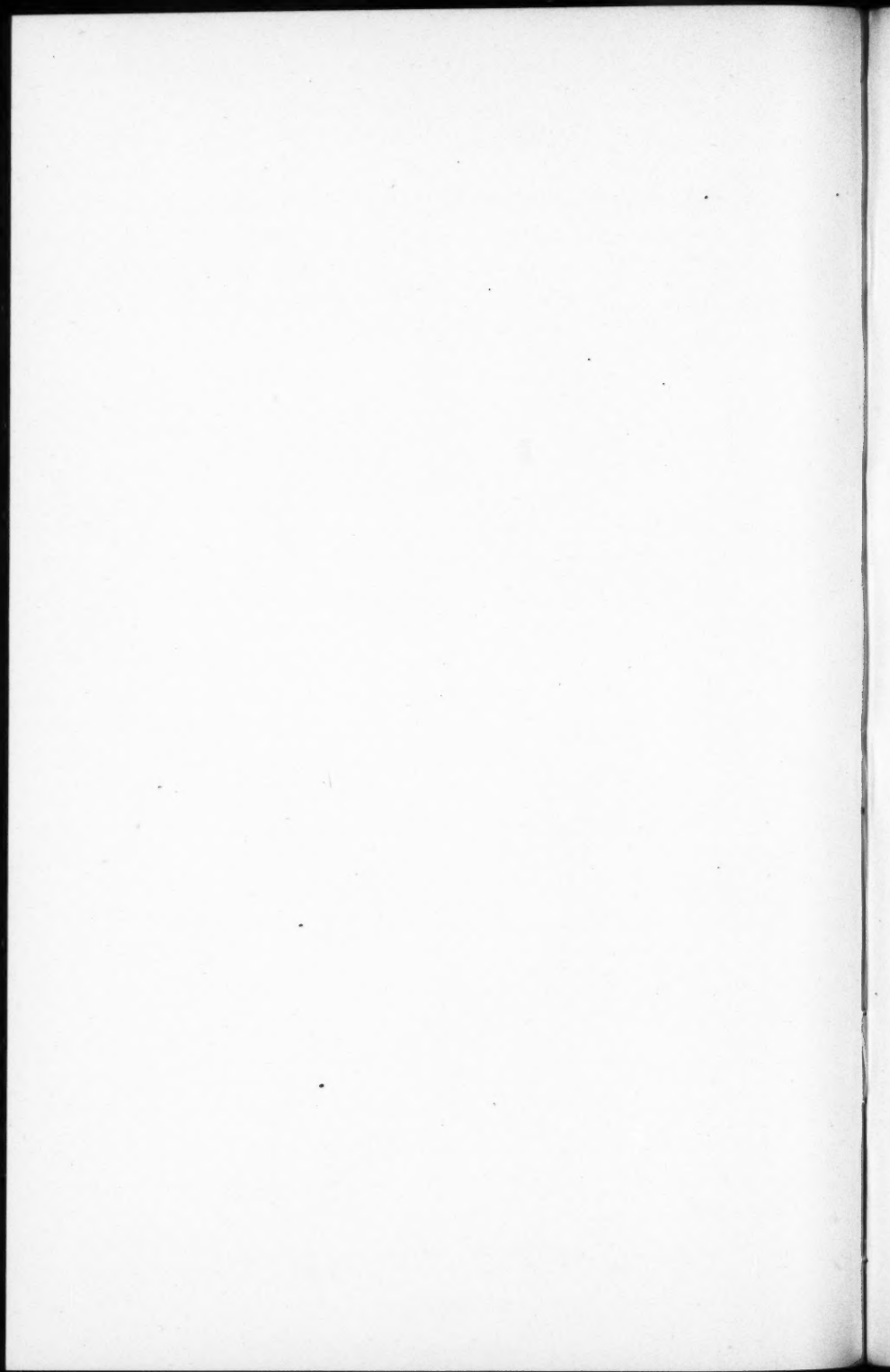
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IN a paper by Grinnell Jones and M. L. Hartmann¹ it was demonstrated that the free energy of formation of silver iodide is greater at 25°C. than at 0°C., thus justifying the inference that the mutual atomic attraction of silver and iodine increases with a rise of temperature, and furnishing, with the aid of Richards'² theory of compressible atoms, a plausible explanation of the hitherto inexplicable fact that silver iodide, when heated, contracts — an almost unique property. But the results, when interpreted with the existing data on the specific heats and heat of formation of the substances involved, are not quantitatively in accord with the requirements of the so-called "Nernst Heat Theorem."

The present paper records the results of an attempt to test the generality of the relations observed by the investigation of another case.

Thallous iodide was selected as the first case to be studied on account of the marked similarity between the iodides of thallium and of silver.

It is true that neither the essential specific heat data nor measurements of the coefficient of expansion of thallous iodide are as yet available, but it is hoped to measure these properties of thallous iodide at the earliest opportunity. The present paper records measurements of the free energy of formation of thallous iodide at 25°C. and at 0°C., together with the results of some subsidiary measurements which were required to interpret these observations. At first an attempt was made to measure directly the free energy of formation of thallous iodide by a method analogous to that used successfully with silver

¹ Grinnell Jones and Miner L. Hartmann, *Jour. Amer. Chem. Soc.*, **37**, 752 (1915).

² T. W. Richards, *Jour. Amer. Chem. Soc.*, **36**, 2417 (1914). This paper gives a summary of the theory and a bibliography of earlier papers.

iodide. An electrolytic cell was prepared, containing as one electrode, metallic thallium coated with thallous iodide immersed in a solution of potassium iodide, and as the other electrode, an iodine electrode. This type of cell, however, proved to be lacking in constancy and reproducibility. After many attempts to overcome its defects, it was reluctantly abandoned. The direct method having failed to give satisfactory results, an indirect method was developed. An electrode of metallic thallium in a saturated solution of thallous chloride was found to give a constant and reproducible potential when atmospheric oxygen was rigorously excluded. From determinations of the conductivity of saturated solutions of thallous chloride and of thallous iodide, conclusions can be drawn in regard to the relative concentration of the thallous ion in these solutions, and hence the potential of thallium in a saturated solution of thallous iodide can be computed. These computations require a knowledge of the mobility of the thallous ion, and therefore the conductivity of a series of solutions of thallous nitrate of progressively increasing dilution was determined. Finally measurements of the potential of an iodine electrode in solutions of potassium iodide of known strength were needed. All the measurements were carried out at both 25°C. and 0°C., these temperatures being selected partly because they are convenient working temperatures and partly because the other data needed are available in the existing literature for these temperatures with sufficient accuracy.

Section 1. The Conductivity of Solutions of Thallous Nitrate from 0.001 N to 0.1 N and the Equivalent Conductance of the Thallous Ion at 25°C. and 0°C.

In 1895 E. Franke³ published measurements of the equivalent conductance at 25°C. of solutions of thallous nitrate and of several other thallous salts. Franke calculated the equivalent conductance of these salts at infinite dilution by extrapolation by Ostwald's "valence and dilution rule." He concluded that the equivalent conductance of the thallous ion at 25° is 71.2 Siemens units. His data, when converted into modern units and extrapolated by Noyes' method, give 75.9 mhos as the equivalent conductance of the thallous ion at 25°C.

Hunt⁴ has measured the equivalent conductance of solutions of thallous sulphate at 18° and 25°C. At 25°C. his data, when extrapolated by Noyes' method, give 156.0 as the equivalent conductance of thallous sulphate, and if the equivalent conductance of the sulphate

³ E. Franke, *Z. phys. Chem.*, **16**, 463 (1895).

⁴ Franklin L. Hunt, *Jour. Amer. Chem. Soc.*, **33**, 795 (1911).

ion be taken as 80, according to Noyes and Falk,⁵ the equivalent conductance of the thallous ion becomes 76.0.

At 18°C. there are measurements on thallous nitrate by Kohlrausch⁶ and von Steinwehr and on thallous sulphate by Hunt. The value 65.9 for the equivalent conductance of the thallous ion at 18°C. has been computed from these measurements⁷ by Noyes and Falk.

We have been unable to find any data from which the equivalent conductance of the thallous ion at 0°C. can be computed.

For the purpose of determining the mobility of the thallous ion the nitrate was chosen as the most suitable salt on account of its ready solubility and the ease with which it can be purified and dried.

The thallous nitrate used for this work was prepared from some thallous sulphate which had been carefully purified by Dr. L. T. Fairhall for other work. To a dilute solution of this salt was added a dilute solution of barium nitrate (free from chloride) in equivalent amounts. The solution was filtered from the barium sulphate, evaporated, the thallous nitrate recovered by crystallization and purified by several recrystallizations with centrifugal drainage. Finally the thallous nitrate was melted in platinum. The melt was clear and colorless and there was no indication of decomposition. Careful qualitative testing gave negative results for barium, sulphate, thallic salts, and halogens. A positive test for nitrite was given by the very delicate alpha-naphthylamine-sulphanilic acid reaction. A repetition of this test quantitatively showed that the nitrite present was not over 0.01%—an amount which could not influence the conductivity by a significant amount. A solution of the salt was neutral to litmus and to phenolphthalein. Spectroscopic examination of the purified thallous nitrate revealed only the characteristic green thallium line $\lambda = 535$ and very weak lines of sodium.

The conductivity cells were of the pipette type and were four in number with cell constants 3.058, 0.5610, 0.05316, and 0.0104 at 25°C. The cell constants were determined independently by two observers in accordance with the method of Kohlrausch, using potassium chloride at both 25°C. and 0°C. A small Leeds and Northrup motor-generator

⁵ A. A. Noyes and K. G. Falk, *Jour. Amer. Chem. Soc.*, **34**, 479 (1912).

⁶ F. Kohlrausch and H. von Steinwehr, *Sitzungsber. kgl. pr. Akad. Wiss. Berlin*, **26**, 581 (1902).

⁷ J. F. Spencer, *Z. phys. Chem.*, **76**, 360 (1911), has computed the conductance of thallous nitrate solution at 25°C. from the data of Kohlrausch and von Steinwehr at 18°C. using Kohlrausch's temperature coefficient, obtaining 147 as the equivalent conductance of TlNO_3 and hence 76.4 for the thallous ion. Incidentally it may be worth while to call attention to the fact that Spencer's figures for the 0.02 N and 0.05 N solution are incorrect. Spencer attributed the value for the 0.05 N solution to the 0.02 N solution and at the same time introduced a wholly extraneous figure for the 0.05 N solution.

served as the source of alternating current. The bridge, by the same manufacturer, was made with extension coils, by which the wire could be lengthened ten-fold in accordance with the design of Washburn.⁸ The bridge wire and resistance box were carefully calibrated. An electrostatic condenser was used to balance the electrical capacity in the arms of the bridge and was a great help in securing a sharp minimum of sound in the telephone. Measurements were made at both $25.00^\circ \pm 0.1^\circ$ and at 0.00° . The 0.1 N solutions were made up quantitatively by weight and the more dilute solutions made from these. All dilutions were made by weight rather than volume on account of the greater accuracy of this method. The densities of the 0.1 N and 0.05 N solutions were determined at both temperatures and the densities at lower concentrations computed on the assumption that the density is a linear function of the concentration.

Two completely independent series were carried out. The following table shows the results of these measurements.

TABLE I.
CONDUCTIVITY OF THALLOUS NITRATE SOLUTIONS AT 25°C .

First Series						
Density	Wt. Normality	Vol. Normality	Specific conductivity κ observed	Water correction $\kappa \times 10^3$	κ corrected	Λ
1.01926	0.097704	0.09959	0.011620	0.96	0.011619	116.67
1.00823	0.04944	0.04985	0.0061988	0.91	0.0061979	124.34
	0.04944	0.04985	0.0061993	0.91	0.0061984	124.35
(1.00156)	0.019909	0.01994	0.0026348	1.17	0.0026336	132.08
(0.99932)	0.009978	0.009971	0.0013610	0.965	0.0013600	136.39
(0.99820)	0.004995	0.004986	0.00069635	0.78	0.00069557	139.51
(0.99752)	0.001999	0.001994	0.00028498	0.66	0.00028432	142.56
(0.99730)	0.0009999	0.0009972	0.00014460	0.76	0.00014384	144.24
Second Series						
	0.09771	0.09959	0.011618	0.79	0.011617	116.65
	0.04942	0.04983	0.0061960	0.83	0.0061952	124.32
	0.019909	0.01994	0.0026353	0.86	0.0026344	132.12
	0.009978	0.009971	0.0013611	0.79	0.0013603	136.42
	0.004993	0.004984	0.00069597	0.72	0.00069525	139.50
	0.001999	0.001994	0.00028493	0.665	0.00028426	142.53
	0.0009999	0.0009972	0.00014465	0.80	0.00014385	144.25

⁸ E. W. Washburn, Jour. Amer. Chem. Soc., **38**, 2431 (1916).

TABLE II.
CONDUCTIVITY OF THALLOUS NITRATE SOLUTIONS AT 0°C.

First Series						
Density	Wt. Normality	Vol. Normality	Specific conductivity κ observed	Water correction $\kappa \times 10^6$	κ corrected	Λ
1.02344	0.097704	0.09999	0.0064801	0.47	0.0064796	64.80
1.01165	0.04944	0.05002	0.0034680	0.44	0.0034676	69.33
	0.04944	0.05002	0.0034683	0.44	0.0034679	69.335
(1.00458)	0.019909	0.02000	0.0014781	0.59	0.0014775	73.875
(1.00222)	0.009978	0.01000	0.00076408	0.48	0.00076360	76.36
(1.00104)	0.004995	0.005000	0.00039125	0.35	0.00039090	78.18
(1.00034)	0.001999	0.002000	0.00015991	0.31	0.00015960	79.80
(1.00010)	0.0009999	0.001000	0.000081008	0.36	0.000080647	80.65
Second Series						
	0.09771	0.10000	0.0064791	0.37	0.0064787	64.79
	0.04942	0.05000	0.0034663	0.39	0.0034659	69.32
	0.019909	0.02000	0.0014783	0.40	0.0014779	73.90
	0.009978	0.01000	0.00076421	0.38	0.00076383	76.38
	0.004993	0.004998	0.00039109	0.36	0.00039073	78.18
	0.001999	0.002000	0.00015991	0.31	0.00015960	79.80
	0.0009999	0.001000	0.000081049	0.40	0.000080648	80.65

Extrapolation to infinite dilution, using the method of Noyes⁹ both graphically and algebraically (method of least squares), gave the following results:

	0°	25°
1st series	82.486	148.974
2nd series	82.527	148.938
Mean	82.51	148.96

According to Noyes and Falk¹⁰ the mobility of the nitrate ion at 25° is 70.6 mhos and at 0° is 40.7 mhos; hence the mobility of the thallos ion at 25°C. is 78.4 and at 0°C. is 41.8.

⁹ See G. A. Abbott and W. C. Bray, Jour. Amer. Chem. Soc., **31**, 745, and John Johnston, *ibid.*, 1010 (1909); and A. A. Noyes, Carnegie Institution Publication, No. 63 (1907).

¹⁰ A. A. Noyes and K. G. Falk, Jour. Amer. Chem. Soc., **34**, 479 (1912).

The equivalent conductances and degrees of dissociation of thallous nitrate solutions at round concentrations deduced from the above data by interpolation over small intervals are shown in the following table:

TABLE III.
EQUIVALENT CONDUCTANCE AND DEGREE OF DISSOCIATION OF THALLOUS NITRATE SOLUTIONS.

Normality	0° C.		25° C.	
	Equivalent Conductance (mhos)	Degree of Dissociation (%)	Equivalent Conductance (mhos)	Degree of Dissociation (%)
0.1000	64.79	78.52	116.60	78.28
0.0500	69.32	84.01	124.29	83.44
0.0200	73.88	89.55	132.06	88.66
0.0100	76.37	92.56	136.37	91.55
0.00500	78.18	94.75	139.50	93.65
0.00200	79.80	96.72	142.53	95.68
0.00100	80.65	97.74	144.24	96.83
0.00000	82.51	100.00	148.96	100.00

Section 2. The Conductivity of Saturated Solutions of Thallous Chloride and of Thallous Iodide at 25°C. and 0°C. and the Solubility of these Salts.

For the interpretation of the electromotive force measurements to be described in the next section a knowledge of the concentration of the ions in saturated solutions of thallous iodide and of thallous chloride at 0°C. and at 25°C. is required. Measurements were therefore made of the conductivity of the saturated solutions, from which the concentrations of the ions have been computed by the aid of the mobility of the ions which had been determined for the purpose (see Section 1).

The total solubility of thallous chloride at 25° has been determined by several experimenters with good agreement in results. Berkeley's ¹¹ results over a range of temperature extending from 0° to 100° have been plotted in a curve, from which the values for 25° and 0° may be determined by interpolation. His values for the two temperatures,

¹¹ Earl of Berkeley, Phil. Trans., 203A, 208 (1904).

respectively, are 0.0161 and 0.00696 mol per liter. At 25°, Noyes¹² and Geffcken¹³ likewise found 0.0161 mol per liter and Hill¹⁴ found 0.01629. Lewis¹⁵ gives the concentration of the ionized portion of this solution at 25° as 0.0143 mol per liter.

Abegg¹⁶ gives the solubility product of thallos iodide at 25° as 5.8×10^{-8} , corresponding to a solubility of 2.4×10^{-4} mol per liter. At 0° we have found no data for the solubility of thallos iodide.

The technique of the determination of the solubility of a slightly soluble salt has been thoroughly worked out, in particular by Kohlrausch, and later by Böttger.¹⁷ The only innovation adopted in the present work was in the design of the cell, which was a modification of Böttger's¹⁷ and is shown in Figure 1. Two platinum-iridium electrodes were sealed in through one end of the receptacle, in a manner designed to render their position rigidly fixed. The stout sealed-in platinum wires were welded to short copper leads, which extended several cm. into the tube at one end of the cell. These wires were insulated from one another, and at the same time connected with the bridge leads, by surrounding them with two narrow glass tubes and filling the space about these tubes with melted paraffine, which when solidified kept the tubes in position and sealed the openings at their lower ends. Mercury could now be poured into the tubes and the lead wires from the bridge inserted in the usual way. Another method of making connection between the cell and the outer circuit is shown in Figure 1 at A. Here the copper leads passed entirely outside the cell and were bent into hooks as in Kohlrausch's method, the terminating tube of the cell being completely filled with paraffine as before. This modification was not suited for work at 0°, as during the rotation of the cell in the ice-bath the wires became much bent. The other form could be used at both temperatures.



FIGURE 1.

The stopper and neck of the cell were covered with a thin rubber cap during its immersion in the constant temperature bath, and a similar protection was provided for the other end during rotation.

¹² A. A. Noyes, *Z. Phys. Chem.*, **6**, 249 (1890).

¹³ G. Geffcken, *Z. Phys. Chem.*, **49**, 296 (1904).

¹⁴ A. E. Hill, *Jour. Amer. Chem. Soc.*, **32**, 1189 (1910).

¹⁵ G. N. Lewis, and C. L. von Ende, *Jour. Amer. Chem. Soc.*, **32**, 732 (1910).

¹⁶ R. Abegg, *Handb. Anorg. Chem.*, **III**, (1), 424.

¹⁷ W. Böttger, *Z. Phys. Chem.*, **46**, 531 (1903).

The grinding of the stopper was of course made carefully enough so that no grease was needed to make it tight. The material of the cell was sufficiently insoluble so that the specific conductance of the solutions measured did not increase by a significant amount during the period of the experiment.

Two cells were used in these determinations, one for thallous chloride, the other for the iodide. In the first cell the electrodes were lightly coated with platinum black; while in the latter cell the electrodes were of bright, burnished metal, and placed not over 1 mm. apart. The cell constants of these cells were 0.14658 and 0.02969. The rest of the conductivity apparatus was essentially the same as that already described. Temperature control was very important in the matter of obtaining concordant results; at 0°, especially, it was found necessary that the conductivity cell be deeply immersed in the bath of cracked ice and distilled water. The cell was caused to rotate end-over-end by being attached at right angles to a horizontal shaft. The solid within the cell was thus brought into intimate contact with all parts of the solution undergoing saturation. Only a small bubble of air was allowed to remain within the cell on filling.

Thallous chloride for these determinations was prepared from pure thallous nitrate, prepared as described on page 201, by precipitating by means of redistilled hydrochloric acid, followed by repeated washing with conductivity water. The precipitate was not dried, but kept under water in the dark until used. Thallous iodide was prepared from carefully purified thallous nitrate by precipitating with dilute potassium iodide solution. The precipitate is at first flocculent and orange, but on washing and agitation it becomes granular and light yellow. On long exposure to light it takes on a somewhat greenish tinge, but in these experiments the salt was protected against such exposure by a suitable shield above the thermostat and the use of a red heating lamp in the bath. The precipitated thallous iodide was washed with conductivity water many times by decantation, the flask being shaken violently so as to break up the larger particles. Like the thallous chloride, it was allowed to soak in conductivity water in the dark for four months before the rinsing was completed. A small quantity of the moist salt was introduced — more than enough for a number of saturations, however — and rinsed several times with conductivity water; and finally the cell was filled with water, the specific conductance of which was determined at the same time in the "water cell." The rubber caps were affixed to both ends of the cell, and the latter rotated in the constant temperature bath for such

a length of time that further rotation did not alter the specific conductance. This usually did not occupy more than a few minutes, but a considerably longer period was generally employed to insure the attainment of equilibrium. The experimental results follow.

TABLE IV.
CONDUCTIVITY OF SATURATED THALLOUS CHLORIDE SOLUTION.

25°C.			
R cell	Specific conductivity observed $\kappa \times 10^6$	Water correction $\kappa \times 10^6$	Specific conductivity corrected $\kappa \times 10^6$
67.43	2173.8	1.18	2172.6
67.42	2174.0 ₇	1.27	2172.8
67.42	2174.1	1.41	2172.7
Mean			2172.7
0°C.			
(288.63)	0.62	
288.88	507.31	0.62	506.69
288.98	507.12	0.70	506.42
288.98	507.14	0.70	506.44
288.93	507.22	0.70	506.52
Mean			506.5

SOLUBILITY OF IONIZED THALLOUS CHLORIDE.

$$\text{At } 25^\circ, \text{ if } \Lambda_{\text{Tl}^+} = 78.4$$

$$\Lambda_{\text{Cl}^-} = 75.8$$

$$c = \frac{1000g}{\Lambda_{\text{Tl}^+} + \Lambda_{\text{Cl}^-}} = \frac{2.1727}{154.2} = 0.014094$$

$$\text{At } 0^\circ, \Lambda_{\text{Tl}^+} = 41.8$$

$$\Lambda_{\text{Cl}^-} = 41.3$$

$$c = \frac{0.5065}{83.1} = 0.006095$$

TABLE V.
CONDUCTIVITY OF SATURATED THALLOUS IODIDE SOLUTION.

25°C.			
R cell	Specific conductivity observed $\kappa \times 10^6$	Water correction $\kappa \times 10^6$	Specific conductivity corrected $\kappa \times 10^6$
796.02	37.30	0.89	36.41
793.46	37.42	0.96	36.46
791.98	37.49	1.08	36.41
792.12	37.48	1.08	36.40
794.20	37.39	0.97	36.42
Mean			36.42
0°C.			
5480.3	5.418	0.414	5.00
5407.4	5.491	0.484	5.01
5484.3	5.414	0.415	5.00
5493.4	5.405	0.484	4.92
5356.7	5.543	0.552	4.99
5353.2	5.546	0.480	5.07
Mean			5.00

SOLUBILITY OF IONIZED THALLOUS IODIDE.

$$\text{At } 25^\circ, \Lambda_{\text{TI}^+} = 78.36$$

$$\Lambda_{\text{I}^-} = 76.5$$

$$c = \frac{0.03642}{154.86} = 0.000235_2$$

$$\text{At } 0^\circ, \Lambda_{\text{TI}^+} = 41.8$$

$$\Lambda_{\text{I}^-} = 43.4$$

$$c = \frac{0.00500}{85.2} = 0.0000587$$

Section 3. The Potential of the Thallium Electrode at 25°C. and at 0°C.

The earliest work on the thallium electrode is probably that of J. Regnault,¹⁸ who studied the cells: Tl, Tl₂SO₄, ZnSO₄, Zn; and Tl, Tl₂SO₄, CdSO₄, Cd; and Tl, Tl₂SO₄, TlHg_x (unsaturated thallium amalgam made up from 2.04 grams of Tl and 10 grams of Hg). He found that the metallic thallium is electro-positive to cadmium by an amount equal to 8 times the thermo-electric force between copper and bismuth with the junctions at 0° and 100°C. (or about 57 millivolts). Goodwin¹⁹ studied several cells containing thalious chloride or bromide as a depolarizer with electrodes of saturated thallium amalgam. These results, although showing the behavior of these sparingly soluble salts as depolarizers, do not permit the calculation of the normal potential of thallium against any standard electrodes, and need not be discussed in detail here.

The first measurements of the thallium electrode against the normal calomel electrode are those of Neumann²⁰ in 1894, who measured both metallic and amalgamated electrodes in saturated solutions of thalious sulphate, thalious chloride, and thalious nitrate against the calomel electrode. For the combination in which we are specially interested, namely, the cell: Tl, TlCl sat., 1.N KCl, Hg₂Cl₂, Hg; Neumann obtained the value +0.711 volt at 17°.²¹ No special precautions to prevent oxidation were taken. Lewis and von Ende²² have shown that when his results are plotted against the logarithm of the ion concentration they show no regularity and are, therefore, apparently subject to some fortuitous error.

Abegg and Spencer²³ studied the effect of the thalious ion concentration on the potential of the thallium electrode, but their values like those of Neumann show marked deviations from the requirements of the Nernst equation. They used amalgamated thallium electrodes on platinum points. They found for TlHg_x, TlCl sat., 0.1 N KCl, Hg₂Cl₂, Hg; $E = +0.7752$ at 25°. Later work has shown this value to be too low.

Spencer²⁴ has measured the potential of a series of thallium amalgams, varying in composition from 0.001831% thallium up to 55.68% thallium, against metallic thallium at 18°C. For all of the saturated

¹⁸ J. Regnault, *Compt. rend.*, **64**, 611 (1867).

¹⁹ H. M. Goodwin, *Z. physik. Chem.*, **13**, 577 (1894).

²⁰ B. Neumann, *Z. physik. Chem.*, **14**, 219 (1894).

²¹ Throughout this paper a positive sign of the potential indicates that the positive current flows through the cell as written from left to right.

²² G. N. Lewis and C. L. von Ende, *Jour. Amer. Chem. Soc.*, **32**, 732 (1910).

²³ R. Abegg and J. F. Spencer, *Z. anorg. Chem.*, **46**, 408 (1905).

²⁴ J. F. Spencer, *Z. Elektrochemie*, **11**, 681 (1905).

amalgams (varying from 44.6% to 55.68% Tl) he finds the amalgam 0.0008 volt more positive than the metal itself.

Shukoff²⁵ measured (incidentally to some work on thallic diethyl chloride) the potential of a saturated thallium amalgam in a saturated thalious chloride solution against the normal calomel electrode at 25° and obtained +0.727 volt. This result differs only by about one millivolt from the later measurements discussed below.

Kurnakow and Puschin²⁶ have investigated the freezing points of a series of thallium amalgams. They find a maximum in the liquidus curve at 15.0°C. with 33.33 atomic per cent. of thallium and two eutectic points at -60°C. with 8.34% thallium and +3.5°C. with 40% thallium. These authors conclude that thallium forms a solid compound, TiHg_2 . As will be pointed out below, this work of Kurnakow and Puschin has been discredited by later investigators.

Sucheni²⁷ has measured the potential of a series of thallium amalgams in contact with 0.1 N potassium chloride saturated with thallium chloride, against the decinormal calomel electrode. He was interested principally in unsaturated amalgams but states that saturated two-phase amalgams have the same potential as metallic thallium. Contrary to his expectations based upon Kurnakow's work, he failed to find a break in the concentration-potential curves at the point corresponding to the compound TiHg_2 . Accepting the existence of the compound TiHg_2 as proved by the work of Kurnakow, he concludes that Tl and TiHg_2 form no solid solutions but that Hg and TiHg_2 form solid solutions. (It will be shown below that this conclusion is incorrect, because based upon the erroneous work of Kurnakow.) Sucheni found the potential of the cell: TiHg_x , TiCl sat., 0.1 N KCl, 0.1 N KCl, Hg_2Cl_2 , Hg; containing a saturated two-phase amalgam, to be +0.830 volt at 37° and +0.820 volt at 0°. The interpolated value for 25° is +0.827 volt.

Some measurements (unpublished) were made by R. W. Kent (1906) in this laboratory upon the thallium metal and amalgam electrodes in solutions of N/10 thalious sulphate at 25°. His cell consisted of: Tl or TiHg_2 , 0.1 N Ti_2SO_4 , 0.1 N NaNO_3 , 1. N KCl, Hg_2Cl_2 , Hg. His corrected measurements, recorded to millivolts, for the metal electrodes — electrolytically prepared metal was used — varied from 0.685 to 0.690 v., with an average of 0.689 v. The degree of dissociation of thalious sulphate is here 61.5% (data of Hunt²⁸), from

25 J. Shukoff, Ber., **38**, 2691 (1905).

26 N. S. Kurnakow and N. A. Puschin, Z. anorg. Chem., **30**, 86 (1902).

27 A. Sucheni, Z. Elektrochemie, **12**, 726 (1906).

28 F. L. Hunt, Jour. Amer. Chem. Soc., **33**, 795 (1911).

which the normal potential of thallium is calculated to be 0.617 volt. The average value for the amalgam electrode was 0.690 volt, corresponding to a normal potential of 0.618 v. The variations in potential in Kent's measurements were, however, of the order of millivolts; and, furthermore, no especial precautions appear to have been taken to avoid oxidation.

Brislee,²⁹ working at room temperature, approximately 17°, but without a thermostat, measured the potential of thallium metal bars in solutions of thalious chloride, thalious nitrate, and thalious hydroxide, separated from the tenth-normal calomel electrode by saturated solutions of ammonium nitrate. He bubbled hydrogen through the solution about the thallium electrodes during measurements. For the cell; Tl, 0.01 N TlCl, NH_4NO_3 sat., 0.1 N KCl, Hg_2Cl_2 , Hg; he obtained 0.773 v. This corresponds to a normal potential of 0.602 volt. Using the temperature coefficient of the normal potential of the thallium electrode, as determined by our experiments, the interpolated value for the normal potential at 25°, according to Brislee, would be 0.612 v.

Much more important than any of the work referred to above is the investigation of G. N. Lewis and C. L. von Ende.³⁰ First, they investigated the influence of changing concentration of thalious ion on the potential of an unsaturated thallium amalgam. They found that, when adequate precautions were taken to prevent solution of thallium from the amalgam by atmospheric oxidation, the observed potentials, in the case of dilute solutions (0.002 N to 0.0333 N), are in almost perfect accord with the Nernst equation. However, with 0.1 N thalious nitrate solution they find a deviation of about one and one-half millivolts, as is to be expected by analogy with many other similar cases. In other words, in dilute solutions the electromotive "activity" of the ions is the same as its concentration as computed from the conductivity. "Instead then of finding any anomaly in the electromotive behavior of thalious ions, we may assert that the Nernst equation holds for the thallium electrode over a large range of concentration with greater accuracy than it has as yet been shown to do in the case of any other electrode." The conflicting observations of Neumann and of Abegg and Spencer are ascribed to insufficient experimental precautions to prevent oxidation. Lewis and von Ende then measured the normal potential of the thallium electrode. They say, "In order to determine the absolute electrode potential of

²⁹ F. J. Brislee, *Trans. Faraday Soc.*, **4**, 159 (1909).

³⁰ G. N. Lewis and C. L. von Ende, *Jour. Amer. Chem. Soc.*, **32**, 732 (1910).

thallium, we must use an electrode of pure metallic thallium or some electrode that is its equivalent. It was shown by Kurnakow and Puschkin³¹ [*sic*] that thallium and mercury form no solid compound above 15°. Sucheni³² showed that mercury does not dissolve to any extent in solid thallium, and that a saturated solution of thallium in mercury therefore has the same potential as pure thallium. This fact, which we have also corroborated,³³ enables us to use a paste of thallium and thallium amalgam in place of solid thallium, which like all solid metals gives an inconstant potential owing to uncontrollable surface variations." They found the potential of a saturated two-phase amalgam in contact with a saturated thalious chloride solution measured against the normal calomel electrode to be 0.7257 volt at 25°C. The normal potential of the thallium electrode is computed to be 0.6170 volt.

However, since this paper of Lewis and von Ende was published, the work of Kurnakow and Puschin, on which they relied, has been discredited by three independent investigations. P. Pavlovich,³⁴ in a repetition of the work of Kurnakow and Puschin, finds, as did the earlier workers, a eutectic at -60°, corresponding to 8 at. per cent. thallium; another eutectic at +2°, with 40% thallium; but his dystectic occurs at 14.8°, covering a range of from 28.7 to 29.7 at. per cent. thallium. Pavlovich postulates the existence of the compound $TlHg_3$, and notes that solid solutions separate between the limits 21 to 31% Tl, as well as between 86-100 at. per cent. Tl.

G. D. Roos³⁵ has also repeated the work of Kurnakow and Puschin on the freezing points of thallium amalgams and obtains results of a quite different character. He finds that the solid compound of thallium and mercury has the formula Tl_2Hg_3 instead of $TlHg_2$. This compound forms solid solutions with both excess of mercury and of thallium within the limits 20% Tl and 31.3%³⁶ Tl. Of more importance for the present purpose, however, is the proof by measurements of eutectic halts in the cooling curves, that metallic thallium forms solid solutions with mercury, which may contain as much as 18% of mercury at the eutectic temperature, which was found to be +0.6°C. instead of 3.5°C. as observed by Kurnakow and Puschin. The work

31 N. S. Kurnakow and N. A. Puschin, *Z. anorg. Chem.*, **30**, 86 (1902).

32 A. Sucheni, *Z. Elektrochemie*, **12**, 726 (1906).

33 No details of this corroboration are given.

34 P. Pavlovich, *Jour. Russ. Phys. Chem. Soc.*, **47**, 29 (1915); *Bull. Soc. Chim.*, **20**, 2 (1916).

35 G. D. Roos, *Z. anorg. Chem.*, **94**, 369 (1916).

36 Atomic percentages; in the present case nearly equal to percentages by weight.

of Roos shows that the two phases present in the eutectic mixture are Tl_2Hg_5 , containing sufficient excess thallium in solid solution to bring its composition up to 31.3% Tl, and solid thallium, containing 18% of mercury in solid solution.

Richards and Daniels,³⁷ in the course of an extensive investigation of the thermodynamic properties of unsaturated thallium amalgams, have also measured the freezing points and electromotive force of a series of thallium amalgams, and their results are entirely in accord with the later independent work of Roos, but not in accord with those of Kurnakow and Puschin. Although Richards and Daniels did not measure the cooling curves of these amalgams and therefore do not confirm this part of Roos' work directly, they have shown by direct comparison that the electromotive force of metallic thallium is not the same as the electromotive force of a two-phase thallium amalgam. At 20°, Richards and Daniels find the potential of metallic thallium to be 2.49 millivolts more negative than the potential of the two-phase amalgam.

Sucheni's results, on which Lewis and von Ende relied in part, do not justify the conclusions which Sucheni drew from them. He measured the potential of a series of thallium amalgams in contact with a 0.1 N potassium chloride solution saturated with thallium chloride against the decinormal calomel electrode. "The potential values, which are given later, represent the mean of several series in which measurements were made through the entire series of amalgams from 0% Tl to 100% Tl. The individual values for the same thallium content differ from each other in the different series by from 0.001 to 0.004 volt. Up to 100% Tl the value remains constant at 0.830," (i.e., from a Tl content of 49.17%, which is shown in his table of results — for 37°C — to have a potential of 0.830 volt, whereas an amalgam of 43.59% and all weaker amalgams are shown to have a lower potential). Therefore his statement that the potential of thallium metal and that of a two-phase amalgam at 37°C. agree, means only that they are within four millivolts of each other. "The electromotive force, as one perceives from the measurements, remains constant from the point where the potential curve becomes horizontal up to pure thallium. From this it follows that in all these amalgams which contain over 43 atomic per cent. of thallium, thallium is present as an independent phase and that thallium does not appreciably dissolve the compound TlHg_2 ." ³⁸

³⁷ T. W. Richards and F. Daniels, *Jour. Amer. Chem. Soc.*, **41**, 1765 (1919). This work was completed in 1914, but the publication was delayed by the war.

³⁸ A. Sucheni, *Z. Elektrochemie*, **12**, 729 (1906).

In his measurements at 0°C . he finds a constant potential of 0.820 to 0.8195 volt from 49.66% thallium down to amalgams containing 31.81% thallium, whereas an amalgam containing 28.44% thallium shows a potential of 0.816 volt followed by a rapid drop to 0.782 volt for a solution containing 21.22% thallium.

In the interpretation of these results his reasoning is based on the premise that the compound TlHg_2 exists (as indicated by the results of Kurnakow and Puschin). The absence of any break in the concentration-potential curve at 33 $\frac{1}{3}$ % thallium (corresponding to TlHg_2) he regards as proof that all mixtures containing more than 33 $\frac{1}{3}$ % thallium at 0° are mixtures of pure TlHg_2 and pure thallium and that no mixed crystals are produced, whereas TlHg_2 and Hg form solid solutions in all proportions. However, since his premise based upon Kurnakow's result has been shown to be in error, this reasoning has no force. His experimental results are, however, entirely in accord with the data of Roos and of Richards and Daniels. According to these experimenters the solid compound is Tl_2Hg_5 (28.57% Tl) which can (according to Roos) form solid solutions with thallium up to the limit 31.3% thallium. Similarly solid thallium can form solid solutions with mercury containing up to 18% mercury or 82% thallium. The eutectic mixture which freezes at $+0.6^{\circ}\text{C}$. would therefore consist of a mixture of two solid solutions containing respectively 31.3% and 82% of thallium. Any amalgam whose total analytical composition fell between these limits would at 0° be made up of these same two phases in proportions which depend upon the composition and would, therefore, be expected to show a constant potential. On the other hand any amalgam containing less than 31.3% thallium but more than 20% thallium would be a single solid phase which would have a potential dependent on the composition. The experimental results of Sucheni are thus entirely in accord with the data and interpretation of Roos, though not in accord with his own interpretation thereof.

This argument will be made clear by an inspection of Figure 2. In the uppermost curves are plotted the results of Kurnakow and Puschin, of Roos, and of Richards and Daniels, on the freezing-points of thallium amalgams. It is very plain that the results of the first mentioned investigators are seriously at variance with those of the more recent workers, and that the wholly independent determinations of Roos and of Richards and Daniels agree very closely over the range covered by the latter.

The curve of eutectic halts, plotted from the results of Roos, shows two intervals in which the halt is vanishingly small; indicating the

existence of solid solutions, formed, on the one hand, by Tl_2Hg_5 with both excess of thallium and excess of mercury, and on the other hand by thallium and mercury.

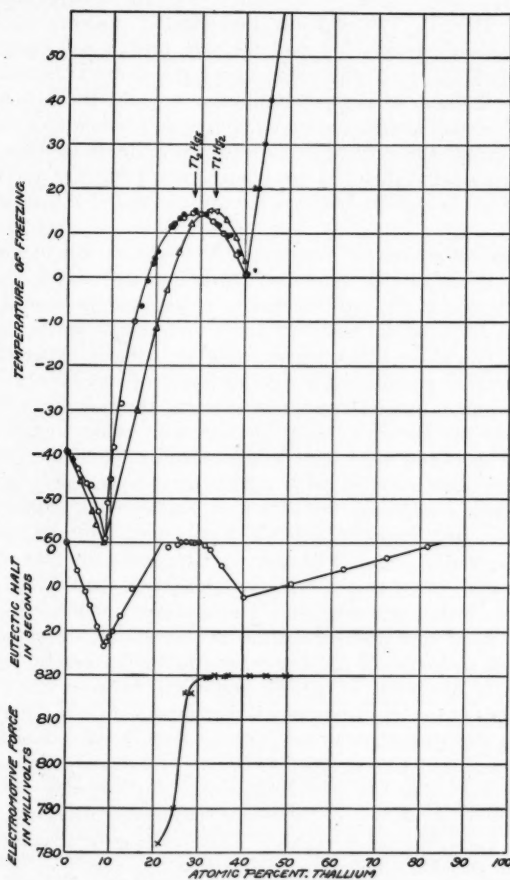


FIGURE 2. Triangles indicate values of Kurnakow and Puschin; black circles, those of Richards and Daniels; white circles, those of Roos; crosses, those of Sucheni.

The lowest curve shows the results of Sucheni on the potential of thallium amalgam electrodes at 0° (measured against the decinormal calomel electrode). The sharp break in the curve occurs very close to the point on the horizontal axis indicated by the composition of the compound, Tl_2Hg_5 . The evidence cited strongly supports the following conclusions: (a) mercury and thallium form a solid compound Tl_2Hg_5 (not TlHg_2); (b) this compound can dissolve excess of either mercury or thallium within definite limits; (c) solid thallium forms a solid solution with mercury up to a limit roughly indicated to be 18% of mercury; (d) the eutectic mixture which is stable at 0°C . cannot contain pure solid thallium as one phase; (e) a two-phase solid amalgam would not be expected to have the same potential as pure metallic thallium.

In our investigation we determined to avoid the use of amalgam electrodes, if metallic electrodes could be obtained which would be constant, reproducible, and reversible. Although the metallic electrodes first prepared did not meet these tests satisfactorily, the difficulty was traced to atmospheric oxidation. After apparatus was developed which permitted the rigid exclusion of atmospheric oxygen from all contact with electrodes or solution the metallic electrodes proved to be satisfactory. Many of them were measured at intervals for several days and did not vary more than 0.2 millivolt. Each of the measurements recorded below refer to an independent experiment. Between each experiment the cells were completely dismantled and set up again with fresh thallium electrodes, new solutions, and new calomel electrodes. As will be seen, variations of more than 0.2 millivolt are rare. Most of the cells contained two thallium electrodes side by side in the same solution. This arrangement made it possible to pass a small current between the two electrodes, thus polarizing one of them cathodically and the other anodically, thereby causing a difference of potential of several millivolts between them. This polarization, however, disappeared completely on standing or on rinsing the electrodes with a fresh solution, thus showing the electrodes to be reversible. In our first series of experiments no amalgam electrodes were used but two metallic thallium electrodes in contact with a saturated solution of thallic chloride were measured against a tenth-normal calomel electrode. These cells gave a value for the normal potential 2.6 millivolts higher than the result of Lewis and von Ende. We, therefore, determined to make a direct comparison of a metallic electrode and an amalgam electrode prepared according to the method of Lewis and von Ende. As will be seen in the table

below the metallic electrode at 25°C. proved to be 2.8 millivolts more negative than the saturated amalgam electrode in the same solution. At 0°C. the difference was 1.8 millivolts in a single measurement. Since the amalgam electrode was discredited by the measurements at 25°C. we were content with a single measurement at 0°C. It may be pointed out that these results are quite in accord with the measurements of Richards and Daniels, who found a difference of 2.49 millivolts at 20°C.

Our value for the potential of the two-phase thallium amalgam electrode at 25°C. is 0.7762 volt, or 0.5 millivolt higher than that of Lewis and von Ende. This difference may perhaps be due to a more

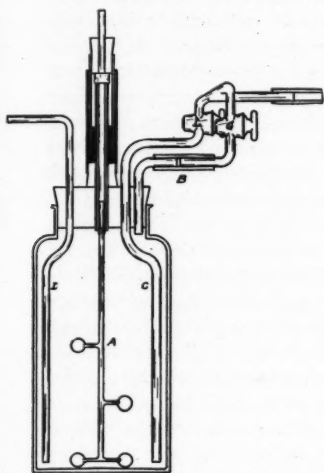


FIGURE 3.

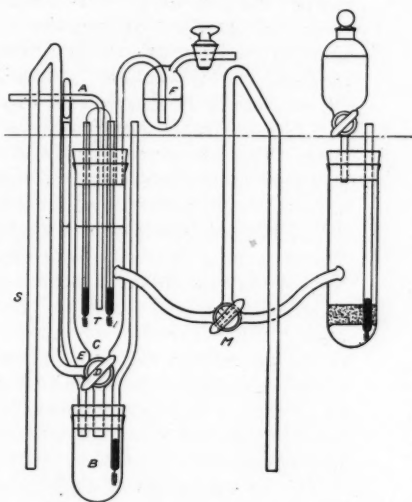


FIGURE 4.

complete exclusion of oxygen in our experiments, or a difference in the purity of the thallium. Our metal was prepared electrolytically, from carefully purified thallos nitrate, whereas Lewis and von Ende used the purest metal they could buy.

Experimental Details.—For the measurement of the potential of thallium against the calomel electrode the apparatus shown in Figures 3 and 4 was devised. The bottle in Figure 3 was employed for the preparation of a saturated solution of thallos chloride at a definite

temperature, in an atmosphere of nitrogen. A wide-mouthed bottle holding about 800 cc., was provided with a rubber stopper, perforated by four holes. Through the central hole passed a glass bearing, containing a closely-fitting brass tube, into which was affixed a glass stirrer (A), which was rotated by a small motor, the vertical shaft of which was attached to the stirrer by several inches of flexible, stout rubber tubing. The bearing was made gas-tight by means of a mercury seal. Through a second hole in the stopper passed an inlet tube for nitrogen gas. Two other tubes, serving respectively for the outlet of the gas or of the solution, passed through the remaining holes of the stopper, and were combined through a T-joint into a single tube, which entered the cell itself. This bottle was completely immersed in a thermostat at 25.00° during the saturation, and pure atmospheric nitrogen gas was permitted to bubble through the solution during this process. For the work at 0° , the bottle and cell were buried in a large tub of cracked ice and water. The stopper of the bottle was thoroughly coated with paraffine before immersion, to render it water-tight. The stirrer was usually allowed to run over night, while a slow current of nitrogen swept through both the bottle and the cell in order to ensure saturation of the solution and absence of oxygen.

The nitrogen generator was kindly loaned us by Dr. A. T. Larson. The removal of the atmospheric oxygen was accomplished in the cold by cuprous ammonium carbonate solution, which was circulated by means of air-lifts through two towers filled with copper chips and gauze. The removal of oxygen is practically complete after passage of the air through the first column; as shown by the fact that the absorbing liquid in the second column remained practically colorless at all times. This generator would deliver a slow stream of gas for many hours, and was frequently allowed to run over night without any attention.

The cell was of special design, shown in Figure 4. The purpose of the apparatus was to permit the plating out of metallic thallium electrodes from a solution of thallous chloride, in the absence of oxygen, and also to permit the rinsing of the cell without access of air, and the refilling of the electrode vessel with thallous chloride solution of definite concentration, as prepared in the saturation bottle. A is the inlet tube for either nitrogen or the solution. If the three-way cock, D, is properly set, and the stopcock of F is open, both the chamber, B, which is used as the anode chamber during the plating out of the thallium electrodes, T, and C, the cathode chamber in this operation, may be filled at the same time. The arrangement shown avoids the

use of a siphon in the plating out process. The thallos chloride solution in B becomes turbid in the vicinity of the platinum anode, but the liquid in C is not contaminated. The siphon-tube, S, is provided so that the cell may be rinsed out with fresh liquid from the saturation bottle without the passage of the liquid through the anode chamber. The rubber stopper of chamber C has four holes, one for the inlet tube, A, one for the outlet tube and trap, F, and two for the thallium electrodes.

The chamber, C, is connected to the calomel electrode chamber by a side-arm, which contains a three-way cock, M. One limb of this cock consists of a siphon-tube, through which, by the adjustment of the stopcock, liquid may be run out from either half of the cell, thus making a fresh junction. The calomel electrode chamber was provided with a small separatory funnel, which served as a reservoir of potassium chloride solution saturated with calomel. The cell when in use was connected to the saturation bottle by means of a short piece of rubber tubing, and could be immersed to the line indicated in the figure, either in the thermostat at 25°, or in a tub of equal size filled with cracked ice and distilled water, for the 0° measurements.

The electrodes themselves consisted of platinum wire, wound into small spirals, and sealed through glass tubes, electrical connection being made as usual with mercury.

Thallos chloride was prepared as already described; see page 206.

Mercury was purified by passing it 20 to 25 times through a five-foot tower of mercurous nitrate solution acidified with dilute nitric acid, followed by redistillation at reduced pressure, allowing a very small current of air to bubble through the liquid during distillation. Part of the mercury thus purified was converted into calomel, by dissolving it in dilute, redistilled nitric acid in the presence of excess mercury, and precipitation of the mercurous chloride by means of dilute, pure hydrochloric acid. The precipitate was washed by shaking up with pure water in a glass-stoppered bottle at least twelve times, decanting the supernatant liquid each time after the precipitate had settled. Then a portion of the solid was placed in a smaller (250-cc.) bottle and the washing continued. The precipitate was now filtered off on a Büchner funnel with the aid of suction, and after a further washing on the funnel, as much of the adhering water as would drain off was allowed to do so, and the moist solid was transferred to a Jena bottle and shaken up several times with approximately 0.1 N potassium chloride solution. Finally it was shaken up with a carefully prepared 0.1 N solution of potassium chloride for about an hour,

a few cc. of purified mercury being added to reduce any mercuric chloride present.

Several series of cells were investigated, in the first of which metallic thallium electrodes in saturated thalious chloride solution were measured against the decinormal calomel electrode, at 25° and at 0°; in the second series, the normal calomel electrode was used, at the same temperatures. The difference in potential between the two series was compared with the difference observed between the decinormal and normal calomel electrodes, at the two temperatures. In the third series of cells, one of the two metallic thallium electrodes was replaced by a saturated thallium amalgam electrode, for the purpose of testing the validity of the assumption that the two have identical potentials under the same conditions.

The measurements were made on a Wolff potentiometer of 20,000 ohms resistance, on the dials of which the e.m.f. could be read off directly to 0.00001 v. The galvanometer was a sensitive instrument of Leeds & Northrup manufacture (type H), and the standard Weston cell had been certified by the Bureau of Standards. The potentiometer was occasionally tested for parasitic and thermoelectric disturbances.

The filling of the calomel chamber involved no new principles. The calomel layer was at least 1 cm. high, and the potassium chloride solution was shaken up at the temperature of the experiment with a calomel-mercury paste for about an hour previous to the filling of the cell. The thallium side of the cell was filled as follows. Referring to Figures 3 and 4: the cock, G, (Fig. 3) was closed and L opened. The pressure of nitrogen thus forced over some of the thalious chloride solution from the saturation bottle into the cell; and if the vent, E, cock, D, and trap, F, (Fig. 4) were opened, the liquid would fill both the lower and upper compartments, B and C, to the desired height — a little below the side-arm. The cock, L, was now closed and G opened, whereupon nitrogen bubbled through both the saturation bottle and the cell, escaping through trap F into the air. The two well-cleaned and ignited platinum electrodes, T, were now connected in parallel to the negative pole of a 16-volt storage battery. The positive lead was introduced into the long tube, through the bottom of which was sealed the platinum anode in chamber B. The stopcock, D, (Fig. 4) was adjusted so that the desired current — as registered by a milliammeter — was obtained for plating out the thallium electrodes. This plating out was continued for a shorter or longer period, according to the strength of the current. Frequently a fraction of a

milliampere was employed and the process allowed to run all night, with a stream of nitrogen passing through the apparatus. When the desired coating had been obtained, the electrolysis was stopped, and stopcock, D, turned so as to shut off communication between chambers B and C. If desired, the anode chamber, B, with its stopper and tubes, could be detached from the rest of the apparatus at this point; but this was not essential.

The rinsing of the thallium electrode chamber was effected by alternately running out the liquid in C through siphon, S, and refilling from the saturation bottle. This necessitated the proper manipulation of the stopcocks, G and L (Fig. 3), and D and F (Fig. 4). When the chamber, C, had been rinsed sufficiently (about six or seven times), it was finally filled almost completely full, together with the side-arm and the bore of the stopcock, M. The cell was now ready for measurement. The test applied to determine whether chamber C had been sufficiently rinsed was to note whether successive rinsings caused any change in the e. m. f. of the cell. An indication of the completeness of removal of oxygen from the chamber was the constancy of e. m. f. after nitrogen had been permitted to bubble through the cell for a short time. The difference between any two thallium electrodes in the same cell rarely exceeded a tenth of a millivolt, and usually was not greater than a few hundredths. This indicates that, when carefully prepared, the metallic thallium electrode is both constant and reproducible.

The amalgam electrodes were of two designs, one of which was described by Sucheni.³⁹ This consisted of a long glass tube, drawn down to a point and sealed at the lower end, and partly filled with a saturated thallium amalgam under water (or paraffine). A long platinum wire was embedded in the amalgam at one end, and sealed through the top of the glass tube at the other. When the electrode was ready for measurement, the tip was broken off and the amalgam exposed. The other form consisted of a J-shaped tube with a small cup at its lower end, containing the amalgam (Fig. 5). This form of electrode permitted more thorough rinsing of the surface of the amalgam. A short platinum wire was sealed through the bottom of the cup in order to make electrical connection between the amalgam and the mercury in the longer



FIGURE 5.

³⁹ A. Sucheni, *Zeit. f. Elektrochemie*, **12**, 726 (1906).

limb of the electrode. The amalgams used contained approximately 55% of thallium. They were heated under water until liquid and then allowed to cool, forming a two-phase amalgam.

The results of these measurements are tabulated below. Each thallium electrode and each calomel electrode were prepared separately, the cell being entirely dismantled between each two determinations. The thalious chloride solutions were saturated anew each time, and fresh materials were also used in making up each calomel electrode; so that the values obtained were entirely independent.

In the work at 0°, the concentrations of the potassium chloride solutions used were adjusted for the change in temperature. The saturation of the thalious chloride solutions at 0° was attained from above as well as below the solubility of the salt at that temperature.

The check measurements at 0° upon the normal and decinormal electrodes were carried out in a cell of the type shown below in Figure 6. The 25° value has been fixed with accuracy by a number of experimenters.⁴⁰

In the following tables each line gives the measurements on an independent cell, the cells being completely dismantled each time and set up again with new electrodes and fresh solutions. The two measurements on each line refer to the two different thallium or thallium amalgam electrodes in each cell measured against the same calomel electrode. The figures given are actual measured potentials without any corrections, the calomel electrode being always positive.

From this table the normal potential of the thallium electrode is calculated to have the following values, which refer to the metal electrode only:

$$\left. \begin{array}{l} \text{At } 25^\circ: E_n = +0.6188 \text{ v.} \\ \text{At } 0^\circ: E_n = +0.5885 \end{array} \right\} \text{against N/1 Electrode.}$$

Lewis, Brighton, and Sebastian⁴¹ in a study of the calomel electrode conclude that the value of the electromotive force between the tenth-normal and the normal calomel electrode at 25° is -0.0529 volt. In

⁴⁰ This enables us to determine the temperature coefficient of the potential difference between the decinormal and normal calomel electrodes over the range 0°-25°; assuming the temperature coefficient to be independent of the temperature in this interval we have: $\frac{-0.0533 - (-0.0489)}{25} = -0.00018$ volt per degree. (See p. 225.)

⁴¹ G. N. Lewis, T. B. Brighton and R. L. Sebastian, *Jour. Amer. Chem. Soc.*, **39**, 2245 (1917).

TABLE VI.

E. M. F. of Cell: Tl, TlCl sat., 0.1 N KCl, Hg₂Cl₂, Hg.

25°C.	
(0.7825)	(0.7825) rejected in computing mean
0.7822	0.7822
0.7820	0.7820
0.7820	0.7821
0.7821	0.7821
Mean	0.7821 volt
0°C.	
0.7583	0.7583
0.7583	0.7582
0.7582	0.7582
Mean	0.75825 volt

TABLE VII.

E. M. F. of Cell: Tl, TlCl sat., 1.0 N KCl, Hg₂Cl₂, Hg and TlHg₂ (sat. amalgam), TlCl sat., 1.0 N KCl, Hg₂Cl₂, Hg.

25°C.	
Tl Amalg.	Tl Metal
0.7264	0.7289
0.7261	0.7290
0.7257	0.7290
0.7262	0.7289
0.7264	0.7291
Mean 0.7262 volt	0.7290 volt
0°C.	
Tl. Amalg.	Tl Metal
0.7084	0.7102
	(0.7107) (0.7109) rejected in computing mean
	0.7102
	0.7102
	0.7102
Mean 0.7084 volt	Mean 0.7102 volt

TABLE VIII.

E. M. F. of Cell: Hg , Hg_2Cl_2 , 0.1 N KCl , 1.0 N KCl , Hg_2Cl_2 , Hg .

	0°C.
	-0.0482
	-0.0480
	-0.0481
	-0.04805
Mean	-0.0481

SUMMARY.

TABLE IX.

Temp.	Cell Measured	No. of deter- min's	Average deviation from mean (volt)	Mean obs'd E. M. F. (volt)	L. J. Potent. calc. (volt)	E. M. F. corr'd (volt)
25°	$\text{Ti} \dots \text{TiCl} \dots 0.1\text{ N.E.}$ (sat.)	8	.00006	0.7821	.0005	0.7816
	$\text{Ti} \dots \text{TiCl} \dots 1\text{ N.E.}$ (sat.)	5	.00006	0.7290	.0007	0.7283
	Difference:					0.0533
	$0.1\text{ N.E.} \dots 1\text{ N.E.}$ ⁴²			0.0529	.0004	0.0533
0°	$\text{Ti} \dots \text{TiCl} \dots 0.1\text{ N.E.}$ (sat.)	6	.00005	0.75825	.0010	0.75725
	$\text{Ti} \dots \text{TiCl} \dots 1\text{ N.E.}$ (sat.)	7	.00006	0.7102	.0017	0.7085
	Difference:					0.04875
	$0.1\text{ N.E.} \dots 1\text{ N.E.}$	4	.00006	0.0481	.0008	0.0489
25°	$\text{Ti Hg}_x \dots \text{TiCl} \dots 1\text{ N.E.}$ (sat.)	5	.00020	0.7262	.0007	0.7255
0°	$\text{Ti Hg}_x \dots \text{TiCl} \dots 1\text{ N.E.}$	1	—	0.7084	.0017	0.7067

⁴² The value, 0.0529 volt, is taken from G. N. Lewis, T. B. Brighton and R. L. Sebastian, Jour. Amer. Chem. Soc., **39**, 2245 (1917).

1914, Lewis and Randall⁴³ state that numerous investigations in their laboratory had fixed the value of this e. m. f. as -0.0530 v. at the same temperature. This value is uncorrected for the liquid junction potential. While the potential between these two liquids cannot be calculated with accuracy, still, inasmuch as it is not very large, the data at hand for its calculation should be good enough to furnish us with a good check upon our measurements. Calculation according to the Henderson equation gives the value 0.0004 — volt at 25° and 0.0008 — volt at 0° , for this potential. The corrected potential between the two calomel electrodes at 25° thus becomes 0.0533 — v. It will be seen that the difference between the first two cells in Table IX. is exactly the same: 0.0533 v.

Slade⁴⁴ also measured the potential of the normal calomel electrode against the decinormal electrode. Three electrodes of each kind were made up according to the directions given in the handbook by Ostwald-Luther, and measured against one another from time to time. The observed value at 25° was -0.0534 ± 0.0002 volt.

At 0° , we measured by independent experiment the potential between the two calomel electrodes, the normal and decinormal, in a bath of cracked ice and water. The mean of four determinations gave as the value for this combination (see Table VIII) at 0° : -0.0481 volt; so that the corrected value becomes -0.0489 volt, when we take into account the liquid junction as above mentioned. The corrected difference between our two cells at 0° is seen to be 0.0488 volt.

A further check upon the values given in the last column of Table IX is obtained from the following considerations. Richards⁴⁵ found the temperature coefficients of the normal and tenth-normal calomel electrodes to be these:

	Calc.	Found	Diff.
N/1	.00057	+ .00061	+ .00004
N/10	.00075	+ .00079	+ .00004

The difference between the temperature coefficients of the N/10 and N/1 electrodes is seen from these figures to be $.00079 - .00061 = .00018$ volt. This value should be equal to the temperature coefficient of the potential difference observed between the two electrodes as seen in the last column of Table IX, and in turn equal to the temperature coefficient of the difference between the two pairs of cells measured at 25° and 0° . In each case the observed difference is $.0045$ v.; the

⁴³ G. N. Lewis and M. Randall, *Jour. Amer. Chem. Soc.*, **36**, 1974 (1914).

⁴⁴ R. E. Slade, *Jour. Chem. Soc.*, **99**, 1977 (1911).

⁴⁵ T. W. Richards, *Proc. Amer. Acad.*, **33**, 1 (1897).

temperature coefficient of the difference is therefore $-.0045/25 = -.00018$ volt per degree.

Our experiments, therefore, corroborate the estimate made by Lewis and Randall in 1914:—

"The temperature coefficient of the e. m. f. between the decinormal and normal calomel electrodes should be determined more accurately. At present we can obtain only an approximate result as follows: The e. m. f. at 25° we have shown to be -0.0530 v., and at 18° , Sauer has found for the same combination -0.0514 . Hence, for the temperature coefficient we find -0.00023 . If, instead of using Sauer's result, we take 0.0530 at 25° , and assume the e. m. f. of the combination to be proportional to the absolute temperature, then we find -0.00018 for the coefficient. For want of better information we shall average these two values and assume the temperature coefficient to be independent of the temperature."

Following is a summary of values of the normal potential of thallium, including only those results with which the values obtained in the present research may fairly be compared. Starred values are calculated results based on determinations under somewhat different experimental conditions:

TABLE X.

Year	Name	Temp. °C.	Cell	Obs. E.M.F.	E_n 25°	E_n 0°
1894	Neumann	17	Tl, TlCl, ind. salt, N/1 cal.	.711*	.615	
1905	Abegg & Spencer	25	TlHg _x , TlCl, N/10 cal.	.7752*	.613	
1905	Shukoff	25	TlHg _x , TlCl N/1 cal.	.727	.618	
1906	Sucheni	0	TlHg _x , TlCl, KCl (N/10), N/10 cal.	.820*		.588
1906	Kent	25	Tl, Tl ₂ SO ₄ , NaNO ₃ , N/1 cal.	.689	.617-8	
1910	Brislee	17	Tl, (.01N)TlCl, NH ₄ NO ₃ , N/10 cal.	.773*	.612	
1910	Lewis & v. Ende	25	TlHg _x , TlCl, N/1 cal.	.7257	.6170	
1920	Present paper	25	Tl, TlCl, N/1 cal.	.7283	.6188	
		0		.7085		.5885

Section 4. The Potential of the Iodine Electrode at 25°C . and 0°C .

The normal potential of the iodine electrode is the only remaining quantity required for the calculation of the free energy of formation

of thallos iodide. An examination of the existing literature shows that apparently trustworthy measurements of this quantity are available at 25°C., but we were unable to find any measurements at 0°C.

The early potential measurements of Beetz, Doat, Regnault, Peirce, Laurie, Bancroft, and Smale⁴⁶ on various cells containing an iodine electrode need not be discussed in detail, since they either do not permit the computation of the normal potential or when judged by modern standards are very crude and inaccurate. In this early work the influence of ion concentration on electrode potential was not sufficiently appreciated. Moreover, these earlier measurements were carried out before it had been shown by Le Blanc and Noyes⁴⁷ by means of freezing point measurements that iodine dissolves in iodide solutions with the formation of some complex ion, and before Jakovkin⁴⁸ had demonstrated by distribution measurements that the complex ion is a triiodide ion (I_3^-). These conclusions of Jakovkin were confirmed and extended by Noyes and Seidensticker,⁴⁹ who found that in solutions saturated with iodine at 25°C. the amount of triiodide formed is almost exactly half of the original iodide present or equal to the remaining iodide.

Küster and Crotogino⁵⁰ were the first to carry out a systematic study of the potential of the iodine electrode with some degree of accuracy. They measured the potential of a bright platinum electrode immersed in solutions of potassium iodide varying in concentration from 1 N to about 0.001 N containing varying amounts of free iodine against a normal calomel electrode at 25°C.

These measurements were repeated in part by Sammet,⁵¹ who measured the potential of a series of cells containing a platinum electrode immersed in solutions of potassium iodide varying from 1-normal to $\frac{1}{16}$ -normal and saturated with iodine at 25° against a normal calomel electrode at 18°C. This procedure involves an un-

⁴⁶ W. Beetz, *Pogg. Ann.*, **90**, 42 (1853).

V. Doat, *Compt. rend.*, **42**, 855 (1856).

J. Regnault, *Compt. rend.*, **43**, 47 (1856).

B. O. Peirce, *Wied. Ann.*, **8**, 98 (1879).

A. P. Laurie, *Phil. Mag.*, (5) **21**, 409; *Jour. Chem. Soc.*, **49**, 700 (1886).

W. D. Bancroft, *Z. physik. Chem.*, **10**, 387 (1892).

F. J. Smale, *Z. physik. Chem.*, **14**, 577 (1894).

⁴⁷ M. Le Blanc and A. A. Noyes, *Z. physik. Chem.*, **6**, 401 (1890).

⁴⁸ A. A. Jakovkin, *Z. physik. Chem.*, **13**, 539 (1894); **20**, 19 (1896).

⁴⁹ A. A. Noyes and J. Seidensticker, *Z. physik. Chem.*, **27**, 357 (1898).

⁵⁰ F. W. Küster and F. Crotogino, *Z. anorg. Chem.*, **23**, 87 (1900) and F. Crotogino, *Z. anorg. Chem.*, **24**, 247 (1900).

⁵¹ V. Sammet, *Z. physik. Chem.*, **53**, 674 (1905).

certain Thomson effect in the solution as well as the temperature effect on the calomel electrode, and is therefore objectionable. Sammet considers that a correction of -0.004 volts should be applied to his results to make them equivalent to direct measurement against a normal calomel electrode at 25°C . When this correction is applied, his results agree with those of Küster and Crotogino within one millivolt. Sammet then calculated the normal potential of the iodine electrode. In making this calculation, he assumed on the basis of the investigations of Le Blanc and Noyes, Jakovkin, and Noyes and Seidensticker already referred to, that in a solution saturated with iodine, one-half of the original iodide is converted into triiodide (the later work of Bray and MacKay shows that these assumptions are only approximately true). He found a fairly constant value for the normal potential in concentrated solutions but a rapid rise in the dilute solutions, and therefore neglected the results obtained with the dilute solutions. The measurements obtained with the stronger solutions gave a value of -0.341 for the normal potential of the iodine electrode, but the more dilute solutions gave higher values rising to -0.363 with the 0.001 N solution.

Maitland⁵² measured the potential of cells containing less iodine than sufficient to cause saturation, the amount of free iodine being determined by distribution experiments. His results with 0.1 N KI gave a value for the normal potential of -0.3409 , but show a variation with concentration of potassium iodide in the opposite direction to the measurements of Küster and Crotogino. Unfortunately, Maitland's measurements did not extend below 0.1 N potassium iodide.

Lewis and Randall⁵³ report that the value -0.3407 was found by P. V. Farragher, but no details are given beyond the bare statement that this value was obtained with dilute solutions.

So far as we have been able to find, no measurements of this potential at any other temperature have been published. Since the work described above was published, the equilibrium between iodine and dilute (0.001 N to 0.1 N) potassium iodide solutions has been studied more carefully by Bray and MacKay⁵⁴ at 25°C ., and later a similar investigation was carried out at 0°C . by Jones and Hartmann.⁵⁵ These investigations show that the assumptions made by Sammet in his calculation of the normal potential are only approximately true.

⁵² W. Maitland, *Z. Elektrochem.*, **12**, 263 (1906).

⁵³ G. N. Lewis and M. Randall, *Jour. Amer. Chem. Soc.*, **36**, 2264 (1914).

⁵⁴ W. C. Bray and G. M. J. MacKay, *Jour. Amer. Chem. Soc.*, **32**, 914 (1910); and W. C. Bray, *ibid.*, **32**, 932 (1910).

⁵⁵ Grinnell Jones and M. L. Hartmann, *Jour. Amer. Chem. Soc.*, **37**, 241 (1915).

Although the existing data on the potential of iodine electrode at 25° appeared to be unusually reliable, it was necessary for our purpose to measure this potential at 0°C. Since measurements could also be made at 25°C. with little extra effort and since we were primarily interested in the temperature coefficient of this potential, we determined to make the measurements at both temperatures. The temperature coefficient thus obtained may be expected to be more

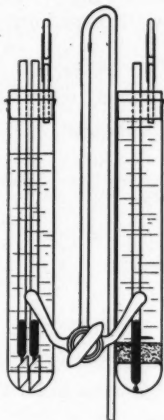


FIGURE 6.

reliable than one deduced by comparison of measurements made by different experimenters, since as far as possible all the conditions except the temperature remain unchanged.

Experimental Details:—The iodine and potassium iodide used were prepared by the method used by Jones and Hartmann.⁵⁶ The solutions were saturated with iodine by long continued shaking with excess of solid iodine at the proper temperature before being added to the cells for the potential measurements. The cells used are shown in Figure 6. The three way cock between the two halves of the cell was closed during the filling of the cell, thus preventing mixing, and also facilitating the formation of a fresh junction by removing solution from both halves of the cell through the siphon tube. The platinum electrodes were about 1. × 1.5 cm. in dimension, and were ignited in a blast lamp immediately before being placed in the cells. A considerable excess of solid iodine was used to ensure saturation. Two

⁵⁶ Grinnell Jones and M. L. Hartmann, *loc. cit.*

electrodes were placed in each cell, thus permitting a test of the reversibility of the electrodes, with results even more satisfactory than in the case of the thallium electrodes. The difference between any pair of electrodes in the same solution in no case exceeded a few hundredths of a millivolt. The measurements were made against a tenth normal calomel electrode instead of a normal electrode, because it was believed that computation of the liquid junction correction would be more reliable than if normal calomel electrodes were used. The following tables show the experimental results:

TABLE XI.

E. M. F. of Cell: Pt, I_2 (solid), 0.1 N KI, 0.1 N KCl, Hg_2Cl_2 , Hg.

OBSERVED E. M. F.

25°C.		0°C.	
Pt Elec. No. 1	Pt Elec. No. 2	Pt Elec. No. 1	Pt Elec. No. 2
-0.2804	-0.2804	-0.2755	-0.2755
-0.2803	-0.2803	-0.2752	-0.2752
-0.2805	-0.2805	-0.2753	-0.2753
-0.2805	-0.2805 ₅	-0.2753	-0.2753
Mean:	-0.2804	Mean:	-0.2753

TABLE XII.

E. M. F. of Cell: Pt, I_2 (solid), 0.05 N KI, 0.1 N KCl, Hg_2Cl_2 , Hg.

OBSERVED E. M. F.

25°C.		0°C.	
Pt Elec. No. 1	Pt Elec. No. 2	Pt Elec. No. 1	Pt Elec. No. 2
-0.2975	-0.2975	-0.2911	-0.2911 ₅
-0.2977	-0.2977	-0.2912	-0.2912
-0.2977	-0.2977	-0.2907	-0.2906
-0.2977	-0.2977	-0.2912	-0.2912
-0.2975	-0.2975	-0.2907	-0.2907
Mean:	-0.2976	Mean:	-0.2909

TABLE XIII.

E. M. F. of Cell: Pt, I_2 (solid), 0.02 N KI, 0.1 N KCl, Hg_2Cl_2 , Hg.

OBSERVED E. M. F.

25°C.		0°C.	
Pt Elec. No. 1	Pt Elec. No. 2	Pt Elec. No. 1	Pt Elec. No. 2
-0.3199	-0.3199	-0.3114	-0.3113
-0.3200	-0.3200	-0.3113	-0.3113
-0.3199	-0.3199	-0.3114	-0.3114
-0.3201	-0.3201-	-0.3114	-0.3114
Mean:	-0.3200	Mean:	-0.3114

TABLE XIV.

SUMMARY OF POTENTIAL MEASUREMENTS ON IODINE CELLS.

Cells Measured: Pt, $\left\{ \begin{array}{l} 0.1 \text{ N} \\ 0.05 \text{ N} \\ 0.02 \text{ N} \end{array} \right\}$ KI solution saturated with iodine, 0.1 N KCl, Hg_2Cl_2 , Hg.

	25°C.			0°C.		
	0.1 N KI I ⁻ conc. I ₂ conc.	0.05 N KI 0.02261 0.00132	0.02 N KI 0.00937 0.00132	0.1 N KI 0.04498 0.000638	0.05 N KI 0.02348 0.000638	0.02 N KI 0.00977 0.000638
Observed potential	-0.2804	-0.2976	-0.3200	-0.2753	-0.2909	-0.3114
Liquid junction correction	-0.0031	-0.0022	-0.0015	-0.0024	-0.0019	-0.0015
Concentration correction	-0.0041	+0.0122	+0.0348	-0.0136	+0.0017	+0.0224
0.1 N calomel electrode:						
1.0 N calomel electrode	-0.0533	-0.0533	-0.0533	-0.0489	-0.0489	-0.0489
	-0.3409	-0.3409	-0.3400	-0.3402	-0.3400	-0.3394

Mean value for cell;

Pt, I₂ molal, I⁻ normal, N. E. at $\left\{ \begin{array}{l} 25^\circ; E = -0.3406 \\ 0^\circ; E = -0.3399 \end{array} \right.$

Or, if we consider cells saturated with solid iodine, we have:

Pt, I₂ sat., I⁻ normal, N. E. $\left\{ \begin{array}{l} \text{at } 25^\circ; E = -0.2555 \\ \text{at } 0^\circ; E = -0.2525 \end{array} \right.$

The normal potential of the iodine electrode shown in table XIV was computed from the observed results by applying three corrections:

(1) The correction for the potential at the junction of the potassium iodide and the potassium chloride solution calculated by the Henderson formula,

(2) the correction for the influence of varying concentration of the iodide ion⁵⁷ and of the free iodine (I₂) according to the Nernst equation:
$$+ \frac{RT}{2F} \ln \frac{(I^-)^2}{I_2}$$
, thus giving the hypothetical potential which

⁵⁷ W. C. Bray and G. M. J. MacKay, Jour. Amer. Chem. Soc., **32**, 914 (1910) and W. C. Bray, **32**, 932 (1910). A small correction has been applied to these results (see Jones' and Hartmann's Table IV, page 251, which gives the figures actually used).

would be observed in a solution in which the concentration of the iodide ion and free iodine is unity, on the assumption that the Nernst equation is valid from the concentration of the measurement up to unity,

(3) a correction for the difference between the tenth-normal and the normal calomel electrode. (See pages 224-225.)

The calculation of the first and of the second corrections requires a knowledge of the concentration and mobilities of the ions present. For the potassium iodide solutions saturated with iodine at 25° this information is supplied by the work of Bray and MacKay⁵⁷ and at 0° by the work of Jones and Hartmann.⁵⁸ Tenth-normal potassium chloride⁵⁹ was assumed to be 85.2% dissociated at 25° and 86.0% at 0°. The mobilities of the ions used in these calculations are as follows:

	25°	0°
K ⁺	74.8	40.1
Cl ⁻	75.8	41.3
I ⁻	76.5	43.4
I ₃ ⁻	41.5	22.8

Summarizing the results of four different experimenters for the potential of solid iodine in a solution normal with respect to iodide ion, calculated for 25°, and referred to the normal calomel electrode, we have:

Küster and Crotogino:	-0.256 v.
Sammet:	-0.256
Maitland: (1) avg. of all solns.	-0.2566
(2) avg. of results with N/10 KI only	-0.2560
Present paper:	-0.2555

In addition, the corresponding value at 0° is determined in the present work as -0.2525 volt.

Section 5. The Free Energy of Formation of Thallous Iodide.

By the aid of the data which we have accumulated in the work described in the foregoing pages, we are now able to carry out the calculation of the free energy of formation of thallous iodide at 25° and at 0°.

This quantity, expressed in terms of electromotive force, will be seen to equal the algebraic sum of the e. m. f.'s of the following combinations:

⁵⁸ Grinnell Jones and M. L. Hartmann, Jour. Amer. Chem. Soc., **37**, 250, 251, 253, 255 (1915).

⁵⁹ A. A. Noyes and K. G. Falk, *ibid.*, **34**, 468 (1912).

- (1) Ti , TiI sat. , TiCl sat. , Ti
- (2) Ti , TiCl , sat. , 0.1 N KCl , Hg_2Cl_2 , Hg
- (3) Hg , Hg_2Cl_2 , 0.1 N KCl , $x \text{ N KI}$, $\text{I}_2 \text{ sat.}$, Pt
- (4) Pt , $\text{I}_2 \text{ sat.}$, $x \text{ N KI}$, TiI sat. , $\text{I}_2 \text{ sat.}$, Pt

Adding: Tl, TlI sat., I₂ sat., Pt

The potential (1) is calculated by the Nernst equation from the measured concentration of the thalious ion in thalious chloride and in thalious iodide.

The potentials (2) and (3) are the directly measured values after applying the liquid junction corrections. The potential (4) is calculated by the Nernst equation from the known concentration of the iodide ion in saturated thallous iodide and in the potassium iodide solutions saturated with iodine.

The free energy of the reaction $\text{TI (solid)} + 1/2 \text{I}_2 \text{ (solid)} = \text{TIH (solid)}$ is evidently F ($= 96,500$ coulombs) multiplied by the sum of these four potentials.

TABLE XV.

25°C.

	volts.		
(1) Tl, TlI sat., TlCl sat., Tl $E = \frac{RT}{F} \ln \frac{0.01409}{0.000235} =$	+0.1051	0.1051	0.1051
(2) Tl, TlCl sat., 0.1 N KCl, Hg ₂ Cl ₂ , Hg $E = \frac{RT}{F} \ln \frac{0.000235}{0.000235} =$	+0.7816	0.7816	0.7816
(3) Hg, Hg ₂ Cl ₂ , 0.1 N KCl, 0.1 N KI, $I_2 \text{ sat., Pt} =$ Hg, Hg ₂ Cl ₂ , 0.1 N KCl, 0.05 N KI, $I_2 \text{ sat., Pt} =$ Hg, Hg ₂ Cl ₂ , 0.1 N KCl, 0.02 N KI, $I_2 \text{ sat., Pt} =$	+0.2835	0.2998	0.3215
(4) Pt, I ₂ sat., 0.1 N KI, TlI sat., I ₂ , Pt $\frac{RT}{F} \ln \frac{0.04267}{0.000235} =$ <i>do.</i> , (0.05 N KI) $\frac{RT}{F} \ln \frac{0.02261}{0.000235} =$ <i>do.</i> , (0.02 N KI) $\frac{RT}{F} \ln \frac{0.00937}{0.000235} =$	+0.1336 1.3038	0.1173 1.3038	0.0947 1.3029
MEAN	1.3035		

TABLE XVI.
0°C.

	volts.		
(1) Tl, TlI sat., TlCl sat., Tl $E = \frac{RT}{F} \ln \frac{0.006095}{0.0000587}$	0.1093	0.1093	0.1093
(2) Tl, TlCl sat., 0.1 N KCl, Hg ₂ Cl ₂ , Hg	0.7573	0.7573	0.7573
(3) Hg, Hg ₂ Cl ₂ , 0.1 N KCl, 0.1 N KI, I ₂ sat., Pt Hg, Hg ₂ Cl ₂ , 0.1 N KCl, 0.05 N KI, I ₂ sat., Pt Hg, Hg ₂ Cl ₂ , 0.1 N KCl, 0.02 N KI, I ₂ sat., Pt	0.2777	0.2928	0.3129
(4) Pt, I ₂ sat., 0.1 N KI, TlI sat., I ₂ , Pt $\frac{RT}{F} \ln \frac{0.04498}{0.0000587}$	0.1563		
	1.3006		
do., (0.05 N KI) $\frac{RT}{F} \ln \frac{0.02348}{0.0000587}$		0.1410	
		1.3004	
do., (0.02 N KI) $\frac{RT}{F} \ln \frac{0.00977}{0.0000587}$			0.1204
			1.2999
MEAN	1.3003		

The free energy (A) of the reaction: Tl (solid) + 1/2 I₂ (solid) = TlI (solid), is obtained from these potentials by multiplying by F (96,500 coulombs); and the heat of formation may be calculated by the Helmholtz equation. The results may be summarized as follows:

	25°	0°
Electromotive force (E)	1.3035 volts	1.3003 volts
$\frac{dE}{dT} =$	+0.000128 volts per degree	
Free Energy of Formation (A)	125.79 kilojoules	125.48 kilojoules
" " " " (A)	30.078 kg. calories	30.005 kg. calories
$\frac{dA}{dT} =$	+12.4 joules per degree	
$\frac{dA}{dT} =$	+2.95 calories per degree	
Heat of Formation (U)	122.11 kilojoules	
" " " (U)	29.198 kg. calories	

Thomsen⁶⁰ found 30,180 cal. for the heat of formation of thalious iodide.

SUMMARY.

1. The equivalent conductance of a series of solutions of thalious nitrate from 0.001 N to 0.1 N was measured at 25°C. and at 0°C. By extrapolation to infinite dilution by Noyes' method the equivalent conductance of the thalious ion at 25°C. was found to be 78.36 mhos, and at 0°C., 41.8 mhos.

2. The conductivity of saturated solutions of thalious chloride and of thalious iodide was measured at 25°C. and at 0°C. The equivalent concentrations of the ionized fraction of these salts, calculated from these results, are as follows:

	25°	0°
TlCl	0.014094	0.006095
TlI	0.000235	0.0000587

3. The potential of the metallic thallium electrode in a saturated solution of thalious chloride was measured against the normal and decinormal calomel electrodes at both 25°C. and 0°C. with the following observed results (uncorrected for liquid junctions):

	25°	0°
Tl, TlCl sat., 0.1 N KCl, Hg ₂ Cl ₂ , Hg; E =	+0.7821 v.	+0.7582 v.
Tl, TlCl sat., 1.0 N KCl, Hg ₂ Cl ₂ , Hg; E =	0.7290	0.7102

From these results the normal potential of the thallium electrode is computed to be +0.6188 volt at 25°, and 0.5885 volt at 0°. It was found by direct comparison that a metallic thallium electrode is more negative than a saturated two-phase amalgam electrode by 2.8 millivolts at 25°C. and 1.8 millivolts at 0°C. This is contrary to the assumption commonly made by earlier investigators of this electrode.

4. The decinormal calomel electrode was measured against the normal calomel electrode at 0°C. with the following results:

Hg, Hg₂Cl₂, 0.1 N KCl, 1. N KCl, Hg₂Cl₂, Hg; E = -0.0481 volt; or, corrected for the liquid junction potential, the difference is -0.0489 volt.

5. The potential of an iodine electrode with solutions of 0.1 N,

⁶⁰ J. Thomsen, Jour. Prak. Chem., 12, 116 (1875).

0.05 N and 0.02 N potassium iodide, saturated with iodine, was measured against the decinormal calomel electrode at 25° and 0° with the following results (uncorrected for liquid junctions):

	25°	0°
Pt, I ₂ sat., 0.1 N KI, 0.1 N KCl, Hg ₂ Cl ₂ , Hg; E = -0.2804 v.	-0.2753 v.	
Pt, I ₂ sat., 0.05 N KI, 0.1 N KCl, Hg ₂ Cl ₂ , Hg; E = -0.2976	-0.2909	
Pt, I ₂ sat., 0.02 N KI, 0.1 N KCl, Hg ₂ Cl ₂ , Hg; E = -0.3200	-0.3114	

From these results the normal potential of the iodine electrode is computed to be:

	25°	0°
Pt, 1 molal I ₂ , 1. N I ⁻ , 1.0 N KCl, Hg ₂ Cl ₂ , Hg; E = -0.3406 v.	-0.3399 v.	

6. From the foregoing results the following results are computed for the reaction: $\text{TI (solid)} + 1/2 \text{I}_2 \text{ (solid)} = \text{THI (solid)}$:

	25°	0°
Free Energy of Formation (A)	125.79 kj.	125.48 kj.
Heat of Formation (U)	122.11 kj.	

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